COLLOIDAL STABILITY OF *PINUS RADIATA* WOOD EXTRACTIVES. PART 2: COMPETING INTERACTIONS BETWEEN WOOD EXTRACTIVES AND PROCESS VARIABLES DETERMINED FROM REGRESSION MODELLING

KAREN R. STACK[1], ELKANA NGWENYA[2], DESMOND E. RICHARDSON[3] and TREVOR W. LEWIS[4]

[1]Research Fellow and corresponding author (karen.stack@utas.edu.au), [2]Lecturer, [4]Senior Lecturer,
University of Tasmania, Hobart, Australia
[3] Senior Specialist, Process Chemistry
Norske-Skog, Boyer, Tasmania, Australia

SUMMARY

This paper presents the results of regression modelling undertaken to investigate the factors affecting colloidal stability of wood extractives from *Pinus radiata*. A factorial experiment was conducted to investigate the effect of process variables such as pH, soluble calcium, temperature, dissolved organic material on the colloidal stability of wood extractives at two different levels of wood extractives representative of the maximum and minimum levels in *P.radiata* extractives. Modelling of the total extractives resulted in poor predictive models. Modelling of the individual wood extracts was found to be more reliable with two way and three way interactions occurring between the process variables. Competing interactions between the process variables and the components were evident.

Keywords: Pinus radiata, wood extractives, colloidal stability, ester to acid ratio, pitch deposition, dissolved organic material

INTRODUCTION

This paper is the second part to a two-part series investigating the colloidal stability of wood extractives from *Pinus radiata*. In the first paper, the effect of wood extractives composition and the interactions with soluble calcium, dissolved organic material (DOM), temperature and pH on colloidal stability and deposition tendency of the wood extractives were explored (*1*). In this second paper, regression modelling was undertaken in an attempt to find a predictive model for deposition tendency based on composition and process conditions, as well as provide a better understanding of the dominant factors, interactions and competing effects between multiple process variables.

Seasonal variation in wood extractive composition has been identified as a key variable in pitch deposition (*2*). During summer months the triglyceride component of the wood extractives has been found to be lower than in the winter months while the fatty acid component follows the reverse trend. The ratio of the triglyceride component to the fatty acid and resin acid components, known as the ester to acid ratio (EAR), has been used by some paper mills as an indicator of colloidal stability (*2*). There is some debate in the literature as to whether this cyclic variation is due to seasonal variations within the lipophilic extractives in the growing tree or due to seasonal variation in lipase activity at the time of felling of the tree or in fact if it is due to storage effects (*3*). Regardless of the cause the fact remains that variation in the composition does occur between summer and winter and these variations greatly influence the phase distribution (*4*), colloidal stability (*1*) and deposition tendency (*5, 6*) of the wood extractives.

Wet end chemistry of the paper machine also has a significant impact on colloidal stability and pitch deposition. The wet end chemistry can be quite complex with many different variables influencing the colloidal stability and deposition behaviour of the wood extractives and other material present in the process water. Considerable attention has been given to understanding these factors such as interactions with dissolved ions (*7-9*), dissolved organic material (*10-13*), process additives (*14-18*) as well as understanding the physical and chemical properties of the wood extractives such as solubility and phase distribution (*19-21*), ionisation (*20-22*), tackiness (*23*), viscosity (*23*) and chemical composition (6, *23*).

The use of modelling and simulation techniques are not new in the pulp and paper industry. Techniques such as regression modelling, analysis of variance (ANOVA), principle component analysis (PCA), partial least squares regression (PLSR), Monte Carlo simulation, and neural networks (ANN) are just some of the statistical techniques commonly used to aid in process control, optimisation and predictive models (*24*). Some limited modelling of the relationship between the amount of pitch deposited and the composition of model wood extractive colloidal dispersions has been carried out (*10, 23*). McLean's work showed that the effect of pitch composition on deposition was greatly influenced by the pH and temperature conditions. The effect of other process variables such as dissolved ions and organic material were not considered in these models. This paper aims to use regression modelling to develop predictive models relating not just deposition tendency but also other aspects of the colloidal stability of the wood extractives to composition and key process variables to better understand the interactions that occur.

EXPERIMENTAL

Materials

Wood extractives (WE) were prepared from *Pinus radiata* TMP pulp samples obtained from Norske Skog Albury Paper mill. Three samples of pulp from the primary refiners in the thermomechanical pulping (TMP) plant were collected at different times of the year and extracted with hexane (LR grade, Chem-Supply) to isolate the wood extractives.

The preparation and the analysis of the wood extractives is described in detail in part 1 of this paper (*1*). Fortification of extract 1 (WE1) and extract 2 (WE2) was required to achieve the desired EAR composition of the wood extractives representative of high and low EAR levels typical of winter and summer periods. To obtain the high EAR extract, additional triolein (Aldrich, technical grade, 65% purity, impurities consist of other triglycerides) was added to extract 1 (WE1) and for the low EAR extract additional abietic acid (Aldrich, technical grade 75% purity, impurities consist of other resin acids) and oleic acid (Aldrich, technical grade, 90% purity, impurities consist of other fatty acids) were added to extract 2 (WE2) as described previously (*1*). The third sample (WE3) that was collected and extracted was used without further addition of other chemicals to alter the composition. This sample (WE3) was used for testing the statistical models.

Table 1 presents the composition of the extract samples used in the experiments and for modelling of the results.

Experimental Design

A factorial experimental design was employed to investigate the effect of various factors and their interactions on the colloidal stability of the wood extractives. Table 2 outlines the variables and proposed levels studied. The target wood extractives (WE) concentration was 100 mg/L.

Table 1: Comparison of composition of prepared wood extractive (WE) colloidal dispersions.

	% fatty acid (FA)	% resin acid (RA)	% triglycerides (TG)	TG:RA:FA ratio	EAR
High EAR extract WE1	6.2+/-2.7	54.5+/-8.8	39.4+/-5.3	6.4 : 8.8 : 1	0.66 +/- 0.09
Low EAR extract WE2	18.5+/-2.4	57.9+/-6.9	23.6+/-4.1	1.28 : 3.1 : 1	0.31+/-0.05
Extract WE3 (test data)	4.0+/-0.7	51.7+/-8.7	43.8+/-5.9	11 : 13 : 1	0.80+/-0.11

Table 2: Summary of variables and proposed levels in the factorial experiment.

Variable	Code	Additions
EAR	A	2 levels - high (0.60) and low (0.29)
DOM:WE ratio	B	5 levels - 0, 0.4, 1, 2, 6
Soluble calcium	C	4 levels - 0, 100, 200, 400 mg/L
pH	D	4 levels - 5.5, 6.5, 7.5, 9
Temperature	E	2 levels - 25°C, 50°C

Experiments were undertaken using a randomised block design. A block consisted of six experiments in which the three different calcium levels were applied at two different pH levels and one temperature, DOM and EAR level. The blocks were randomised to reduce bias and systematic errors. Randomised repeat experiments were also performed to determine reproducibility. A total of 450 experiments were undertaken including repeats.

Statistical Analysis

Statistical analysis and regression modelling of the data was undertaken using STATA 10.0 (StataCorp). The models were created using data from extract WE1 (high EAR) and extract WE2 (low EAR). Backward stepwise linear regression with a significance level of $p< 0.1$ for removal of terms from the model was undertaken. A series of models that included one-way interactions, two-way interactions and three-way interactions between the variables were created.

Extract WE3 was used for model testing. The goodness of fit of the test data (WE3) to the predictive model was determined by calculation of the coefficient of determination R^2.

Regression diagnostics were undertaken to ensure validity of the linear regression modelling assumptions of linearity, normality of residuals and homoscedasticity.

Standardisation of the regression coefficients (also called beta coefficients) in the models was undertaken to compare the effects of the different independent variables measured in different units. The beta coefficient for a particular independent variable with respect to the measured dependent variable was determined by multiplying the unstandardised coefficient in the model for the particular independent variable by the ratio of the standard deviation of that independent variable to the standard deviation of the dependent variable.

RESULTS

Models For Total Extractives

Regression modelling of WE 1 (high EAR) and WE 2 (low EAR) data sets was undertaken to find predictive models for the total extractives in the stable DCS material, deposited material and unstable colloids. A number of models were found and those with the highest R^2 values were then tested using the WE 3 data set. The model with the highest goodness of fit to the predicted model was then chosen. Table 3 presents the models found for predicting the amount of total extractives in the deposited material, unstable colloids, stable colloids and soluble material.

The models for the total extractives deposited, total extractives in unstable colloids and in the soluble material were found to have low R^2 values indicating a poor fit between the predicted model values and the observed measured values. The model for the total extractives in stable colloids had a high R^2 (R^2=0.94), indicating that the model for the total extractives in the stable colloids was able to explain 94% of the variability in the data. However, the root mean square error (RMSE) value, a measure of the difference between the predicted and observed values, was high (RMSE = 15.6) indicating a large degree of variability and uncertainty in the data (Table 3).

Figure 1 compares the fit of the different data sets to the predicted model for the total extractives in the stable colloids. The model data for the stable colloids, based on WE1 and WE2, does not appear to adequately predict the total extractive levels at the low and high concentration extremities: it over-estimates at low concentration and under-estimates at high concentrations. The effect observed is further exaggerated using the WE3 test data set with the model predicting as much as 60 mg/L total extractives at low levels (> 5mg/L) of measured total extractives in the stable colloids. These discrepancies mean the model obtained is not reliable. Similar problems were found with the other models for the total extractives in the deposited material, unstable colloids and soluble material.

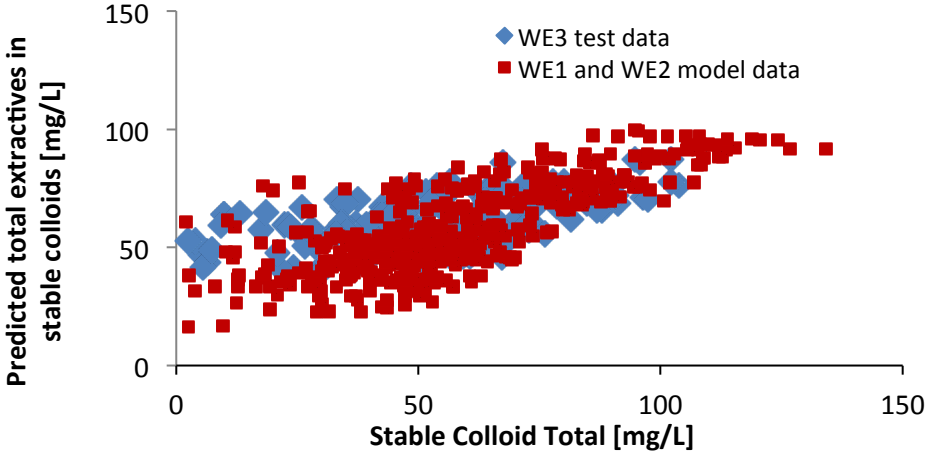

Fig. 1. Comparison of model fitting for predictive model of total extractives in stable colloids.

Table 3: Coefficients (including standard error) for the various models found for total extractives in deposited material, unstable colloids, stable colloids and soluble material.

Variable	Deposited Material [mg/L]	Unstable colloids [mg/L]	Stable colloids [mg/L]	Soluble material [mg/L]
Predeposition Concentration (predep) [mg/L]			0.632 ± 0.060	0.083 ± 0.04
A (EAR)		15.8 ± 4.4	-51 ± 18	
B (DOM: WE ratio)	-3.00 ± 0.70	-0.84 ± 0.39	1.71 ± 0.52	
C (Ca) [mg/L]				-0.062 ± 0.027
D (pH)	-6.5 ± 1.9		21.1 ±3.9	-6.7 ± 2.1
E (Temperature) [°C]	2.40 ± 0.32	0.57 ± 0.19	-2.9 ± 0.4	
A x B				
A x C		0.117 ± 0.042		
A x D			1.19 ± 0.45	5.9 ± 2.5
A x E	5.7 ± 1.3	-1.17 ± 0.44		
B x C		0.0114 ± 0.0036		
B x D				1.6 ± 0.4
B x E	-0.52 ± 0.14	0.106 ± 0.04		-0.23 ± 0.09
C x D	-0.012 ± 0.002	0.0135 ± 0.0025		-0.012 ± 0.003
C x E		0.0010 ± 0.0003		
C x C		-0.00020 ±0.00004		0.00025 ± 0.00005
D x D	0.007 ± 0.002		-2.17 ± 0.35	0.70 ± 0.12
D x E	-0.0010 ± 0.0003	-0.073 ± 0.027	0.28 ± 0.05	0.10 ± 0.03
A x B x D				-2.82 ± 0.6
A x B x E				0.47 ± 0.14
A x C x D		-0.024 ±0.006		0.0069 ± 0.0027
A x D x E		0.103 ± 0.06		-0.20 ± 0.05
B x C x D				
B x C x E		0.0003 ± 0.0001		
B x D x E		-0.012 ± 0.006		
R^2	**0.55**	**0.65**	**0.94**	**0.78**
RMSE	**13.0**	**7.8**	**15.6**	**9.6**
Extract 3 fit *	**0.09**	**-0.073**	**0.11**	**0.87**

*Coefficient of determination for fit of predicted model (based on WE 1 and WE2 data) to extract 3 (WE3) data set (the model test data set)

Models For Individual Components

Modelling of the individual extractive components in the various fractions was also undertaken and these models proved to be more reliable. In order to improve the model and achieve a high R^2 it was found that, for each wood extractive component, terms for the other wood extractive components were needed indicating that an interaction between the components was occurring. Table 4 shows the improvement in R^2 and RMSE when the individual components and their interactions were considered for predicting the amount depositing. It is apparent from the sign of many of the coefficients in the models that the effect of DOM:WE ratio, pH, temperature and EAR on RA behaviour is opposite to the behaviour of TG and

sometimes even the FA. These differences support the idea that there are competing effects between the components and process variables.

Table 4: Coefficients for the various models found for total extractives deposited and individual components in the deposited material.

Variable	Total extractives [mg/L]	RA in deposits [mg/L]	TG in deposits [mg/L]	FA in deposits [mg/L]
A (EAR)		-33.5 ± 7.5	24.5 ± 4.7	9.1 ± 4.6
B (DOM: WE ratio)	-3.00 ± 0.70	-0.69 ± 0.19		
C (Ca) [mg/L]				
D (pH)	-6.5 ± 1.9	2.40 ± 0.74	-1.58 ± 0.52	-1.10 ± 0.34
E (Temperature) [°C]	2.40 ± 0.32	0.36 ± 0.09	-0.154 ±0.071	0.27 ±0.06
FA		1.61 ± 0.14		
RA			0.500 ± 0.023	0.197 ± 0.010
TG		0.89 ± 0.06		
A x B	5.7 ± 1.3		-1.01 ± 0.31	
A x C		0.063 ± 0.017		-0.026 ± 0.008
A x D		3.33 ± 0.96	-2.44 ± 0.65	-1.10 ± 0.63
A x E	-0.52 ± 0.14			-0.44 ± 0.12
B x C	-0.0121 ± 0.0023		-0.0019 ±0.0005	
B x D		0.79 ± 0.15		
B x E		-0.197 ± 0.035	0.0195 ± 0.0057	
C x D	0.007 ± 0.002	-0.0050 ±0.0013		0.0023 ±0.0006
C x E	-0.0010 ± 0.0003			-0.00014 ± 0.00007
D x D	0.74 ± 0.24	-0.29 ±0.09	0.158 ± 0.066	0.153 ± 0.041
D x E	-0.23 ± 0.04	-0.033 ±0.013	0.019 ± 0.009	-0.034 ± 0.008
A x B x C				0.0037 ± 0.0009
A x B x D		-0.90 ± 0.22		
A x B x E		0.285 ± 0.054		
A x C x E		-0.0016 ± 0.0004		0.00056 ±0.00020
A x D x E				0.047 ± 0.017
B x C x D				-0.00046 ± 0.00009
B x C x E				0.000027 ±0.00001
C x D x E		0.00012 ± 0.00003		-0.000031 ±0.000016
R^2	**0.55**	**0.91**	**0.80**	**0.82**
RMSE	**13.0**	**3.4**	**2.7**	**1.2**
Extract 3 fit*	**0.093**	**0.67**	**0.63**	**-2.6**

*Coefficient of determination for fit of predicted model (based on WE 1 and WE2 data) to extract 3 (WE3) data set (the model test data set)

Figures 2 and 3 show the goodness of fit for the models for the resin acids, fatty acids and triglycerides in the deposited material (Figure 2) and stable colloids (Figure 3). The equations for the models are presented in Appendix 1. The predictive models for RA and TG can model the WE3 test data for predicted resin acids and triglycerides in deposited material and resin acids in stable material very well. Modelling of the FA in deposited material and stable colloids was not as good. There are several possible reasons for the poor fit for the FA data. The first is that the FA levels were low and within the range of experimental error of the measurements. The second is that the data for WE1 and WE2 from which the

model was constructed indicates two distinct populations which may in fact be behaving quite differently and the test data only covers a small region of the model and is behaving more like one of the two populations (namely WE1).

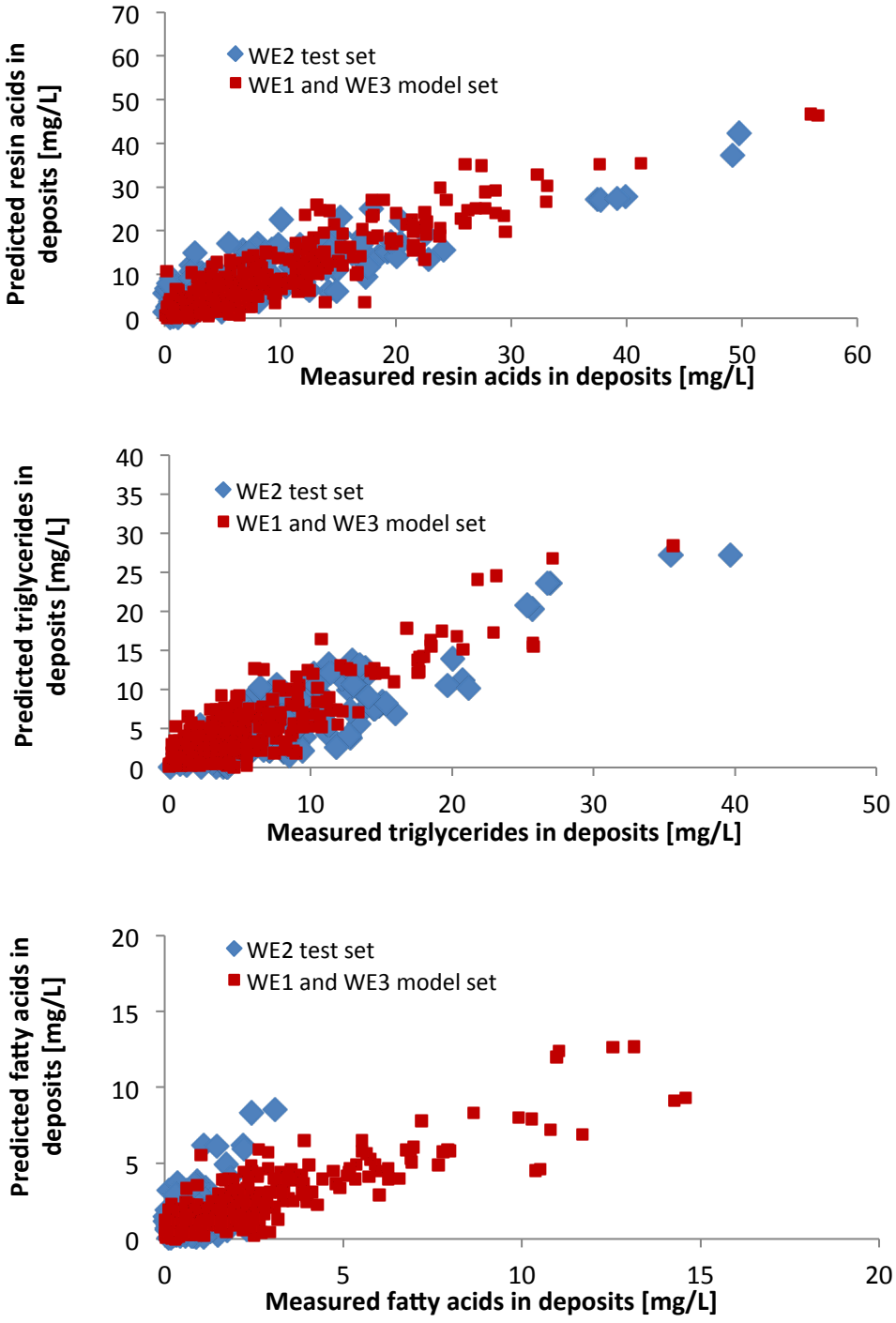

Fig. 2. Comparison of predictive models for deposited material for test data set (WE3) and data set used for modelling (WE1 and WE2).

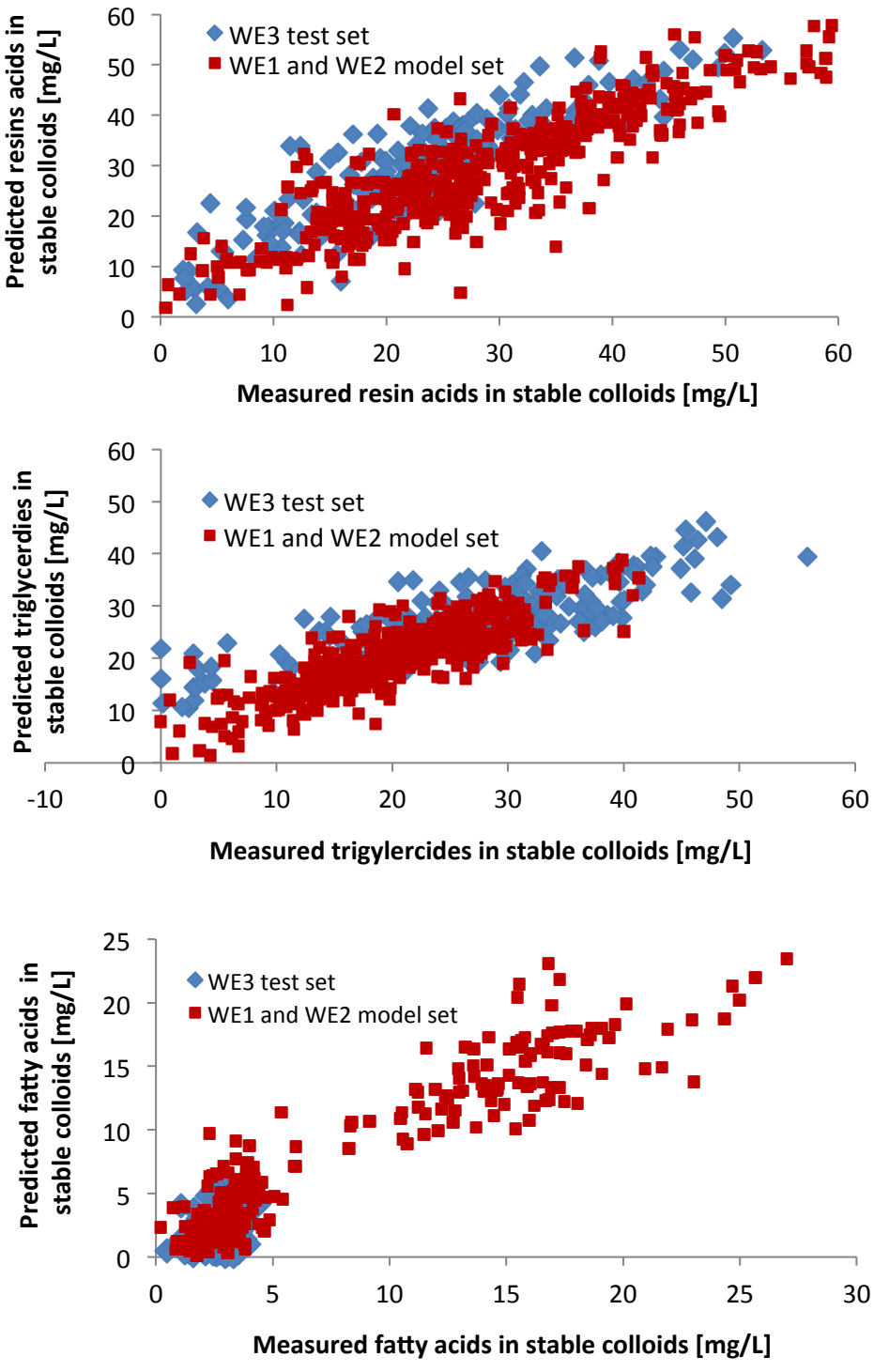

Fig. 3. Comparison of predictive models for material in stable colloids for test data set (WE3) and data set used for modelling (WE1 and WE2).

In order to determine which factors and interactions were having the greatest influence on the deposition behaviour and stability of the individual wood extractive components the standardised coefficients (beta coefficients) for the models were determined and are shown in Figures 4 - 6. The results in Figure 4a, for the resin acids in deposited material, indicate that the interaction with the other components and interaction of pH and DOM : WE ratio (B x D), had the greatest influence followed by the interaction between DOM : WE ratio and temperature (B x E) and pH squared (D x D). For the triglycerides in the deposits (Figure 4b), the EAR (A), amount of RA in the deposits followed by the interaction of EAR and pH (A x D) had the greatest influence. EAR (A) was found to have the greatest influence on the amount of resin acids and triglycerides in the stable colloids (Figure 5). pH level (D x D) was found to also strongly influence the amount of resin acids in the colloids (Figure 5a) while soluble calcium (as a squared term) (C x C) and an interaction between temperature and pH (D x E), along with EAR (A) and the amount of RA, were found to have major influences on the amount of triglycerides in the stable colloids (Figure 5b). EAR (A) and FA concentration were found to have the greatest influence on the amount of resin acids in the unstable colloids (Figure 6a). Soluble calcium (C) was found to be important in determining the amount of triglycerides in unstable colloids (Figure 6b).

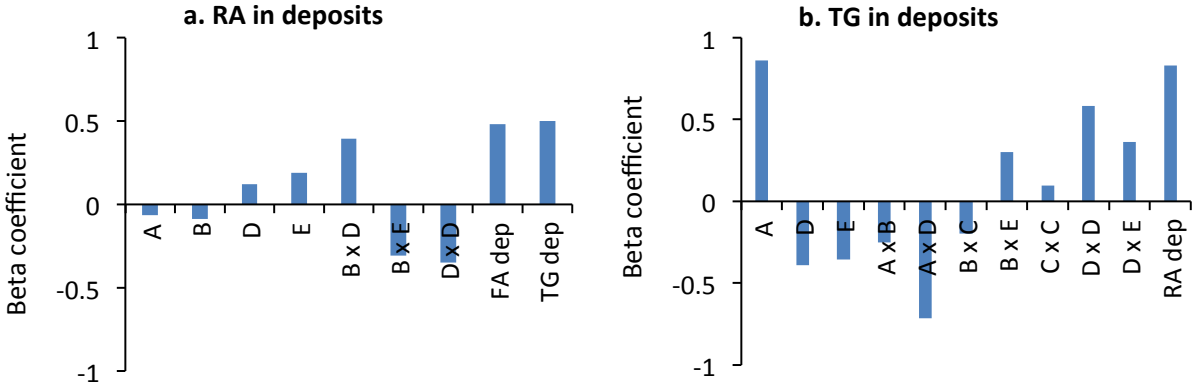

Fig. 4. Influence of factors and interactions on the amount of (a) resin acid and (b) triglycerides in deposits.

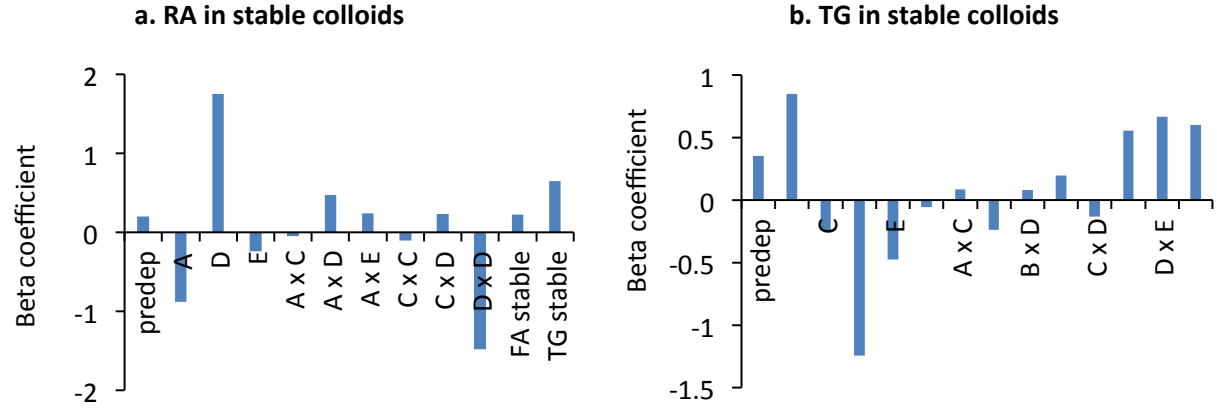

Fig. 5. Influence of factors and interactions on the amount of (a) resin acid and (b) triglycerides in stable colloids.

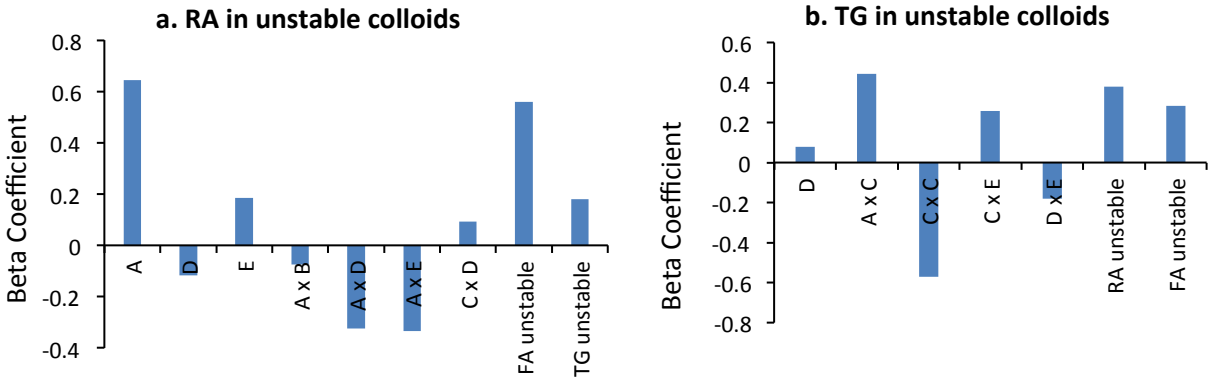

Fig. 6. Influence of factors and interactions on the amount of (a) resin acid and (b) triglycerides in unstable colloids.

DISCUSSION

The models obtained along with the problems identified reinforce the issues associated with studying the deposition and colloidal stability of wood resin extractives. No single simple model predicting the deposition of the wood extractives from the various process variables could be obtained, highlighting the complexity of the system. To obtain reasonable models it was necessary to consider interactions between the variables.

There are several reasons for the problems with the models for the total extractives. These include:

i. Variability found in the test data,
ii. Missing terms or factors not considered in the models,
iii. Competing interactions from the extractive components (TG, RA and FA).

Although all care was taken to reduce variability and experimental error, it was only the models involving variables with a wide range of concentrations, such as in the case of stable colloids, that reliable models could be found. This was not unexpected as for those variables in which the range of concentrations was small, the relative effect of the experimental errors become significant.

The modelling of the behaviour through the individual components highlighted that interaction between components and interactions between the different variables were important. The interaction between components of the wood resins is well known (*6, 25, 26*). Previous modelling work of the deposition behaviour of the wood resins from *P.Radiata* showed that the interaction between the components was important and the models proposed included interaction terms between the components (*6, 25*). McLean (*25*) showed that the interactions that occur are dependent on pH and temperature. He found that at pH 5.5 and 50°C, little interaction between components occurred and the amount of pitch deposited was proportional to the concentration of resin acids in the wood extractive colloids while at pH 7.0 and 50°C, all three components were interacting and contributing to the deposition.

The models for the individual components also showed that competition between the effects were occurring. Competing effects have been noted by Dreisbach (*27*) who reported that resin acid deposition potential was minimal at neutral pH and low temperature whereas fatty acid deposition potential was at a maximum under the same conditions.

Deposition Behaviour Of Resin Acids

The major lipophilic wood extractive component in *P.radiata* is the resin acids, unlike Spruce where triglycerides dominate (28). The resin acids also appear as a major component in pitch deposits occurring from *P.radiata* wood extracts. The model obtained for the amount of resin acid depositing shows a strong influence of pH, DOM : WE ratio and the amount of the other extractive components present as shown in Figure 4. Understanding the interactions that take place is obviously important in order to minimise deposition problems.

In the absence of DOM (ie DOM : WE ratio = 0), the model predicts a quadratic relationship with pH in which a maximum in resin acids in the deposited material occurs at a pH below 5 and a decrease in resin acids in the deposits at pHs above 5, as shown in Figure 7. As the amount of DOM increases the maximum of the pH quadratic relationship shifts to higher pH. As shown in Figure 7, the model predicts that the addition of DOM causes a decrease in the resin acids in the deposits at low pH with the effect being larger for the high EAR pulp (WE1) and an increase in the resin acids in the deposits at high pH with increasing DOM. This implies that the DOM acts to stabilise the colloids at low pH and destabilise them at high pH. Between the pH range of 6 to 8, the effect of the DOM is influenced by the EAR. This is a critical region then for the operation of the paper machine. The model predicts that the low EAR pulp is more susceptible than the high EAR pulp to destabilisation by DOM as the pH increases above 5.5. For the high EAR pulp, the model predicts that DOM is able to stabilise the colloids at pH less than 8 but above pH 8 destabilisation by the DOM is apparent. The reason the DOM interacts in different ways with the high and low EAR is not clear. The amount of soluble resin acids is higher on average in the low EAR pulp and so the effect may be related to interaction between DOM and soluble resin acids resulting in the formation of unstable colloids and aggregates that readily deposit.

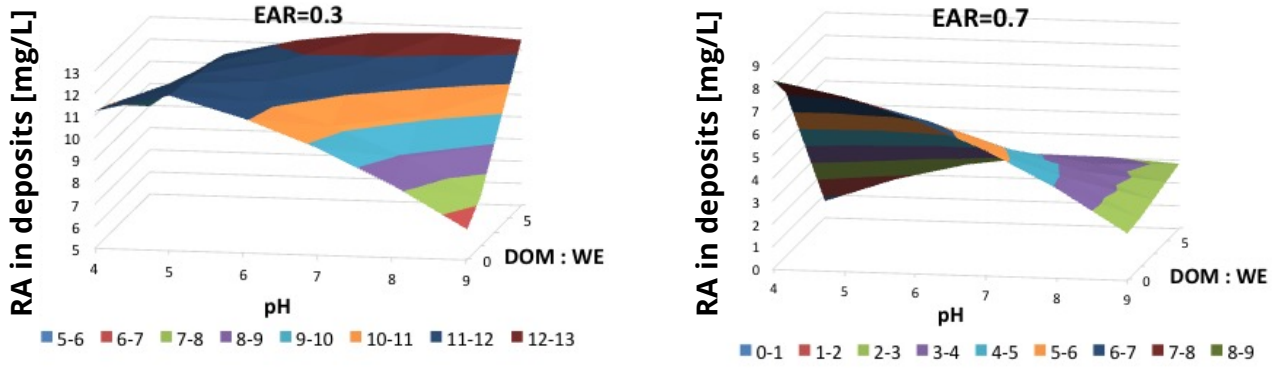

Fig. 7. Surface plot of predicted relationship between pH and DOM : WE ratio on the resin acids in deposits at 50°C for 0.3 EAR and 0.7 EAR. (y axis is colour coded; ranges given in legend)

Deposition Behaviour Of Triglycerides

Triglycerides can also be a significant component in the wood extractives of *P.radiata*. They are the component that has the greatest effect on the observed seasonal variations in the EAR (*25*). The normalised coefficients indicate that EAR (A), pH (D), and amount of resin acid present are the greatest contributors to the triglycerides in the deposited material. A high EAR would indicate a high level of triglycerides in the

extractives and so it seems logical that more triglycerides would be also found in the deposits. The relationship with pH is opposite to that of the resin acids suggesting competing effects. The model indicates a minimum in the triglycerides in the deposits occurs at approximately pH 7 at high EAR and at a pH below 4 in the low EAR pulp as shown in the surface plots of the model in Figure 8. It is also apparent from the surface plots that low EAR pulp (EAR = 0.3) is more sensitive to changes in pH and DOM than the high EAR pulp (EAR = 0.7) in regards to the amount of triglycerides in the deposits.

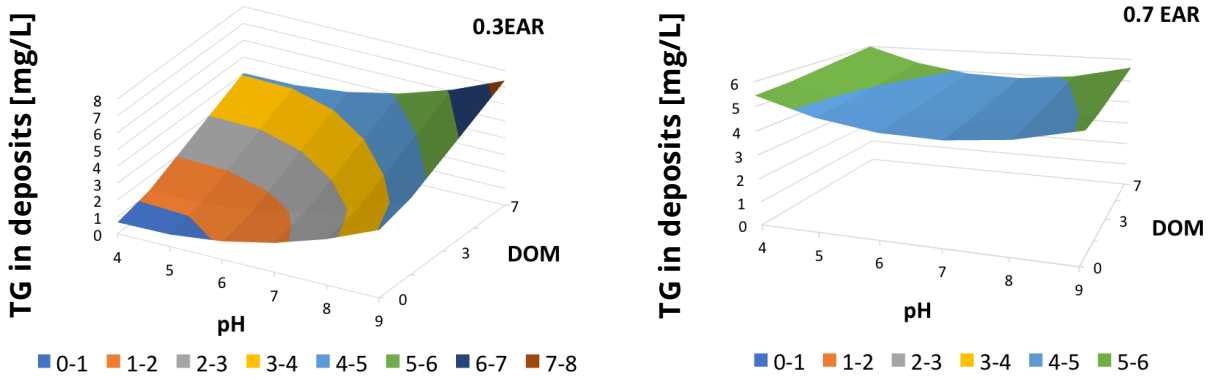

Fig. 8. Surface plot of predicted relationship between pH and DOM:WE ratio for the triglycerides in deposits at 50°C.

Role Of Soluble Calcium

Soluble calcium is known to contribute to destabilisation of wood extractives and increase pitch deposition, as well as interact with resin acids and fatty acids to form metal soaps. The experimental work undertaken in part 1 which provided the data for the modelling showed that deposition significantly increased with the addition of soluble calcium in the absence of DOM and at low pH levels (<6.0) (*1*). So it was expected that soluble calcium would be one of the key variables in the models. This however did not prove to be the case. The only models in which soluble calcium appeared to have a major influence was in the triglycerides and fatty acids in the unstable colloids. One of the reasons it did not appear or only had a small influence in the models is because the effects were being overshadowed by the influences of the other variables such as DOM and pH. The experimental region over which soluble calcium was observed to be significant (0 DOM and pH 5.5) was only a small region of the experimental space and so its influence on the entire experimental space was small. The models for resin acids in stable and unstable colloids had interaction terms with calcium indicating it was having some effect but the other terms in the model appeared to have a greater influence based on the magnitude of the beta coefficients (Figures 5a and 6a).

Soluble calcium appeared to have a greater effect on the fatty acids and triglycerides in the unstable colloids than the resin acids, which was surprising. The effect on the fatty acids was expected as fatty acids are known to form insoluble soaps with calcium. The effect with the triglycerides however was interesting. Care is needed in interpreting the models as correlation does not imply causality. The model does not necessarily mean that calcium is directly interacting with the neutral triglycerides and causing them to destabilise and deposit, but may just be indicating that calcium plays a role in some way. Strand *et.al.* found that when calcium was added to a wood extractive suspension, the resin acids were not removed from the water phase to the same extent as the fatty acids and triglycerides (*29*). They suggested that the calcium resinates formed had a higher solubility than the calcium salts of the fatty acids. This may then explain why

no effect from calcium in the models was observed for the resin acids. Strand's observation however for the triglycerides is in line with the results predicted from the model. Although no explanation for the behaviour of the triglycerides was given by Strand, it is possible that, because the triglycerides followed the same trend as the fatty acids in Strand's work, the effect was a result of an interaction between the triglycerides and fatty acids. The models do predict a strong influence from the amount of fatty acid and resin acids present in the unstable material having a large impact on the amount of triglycerides. Work by Lee (*30*) using EPR to probe the internal structure of the wood resin colloid found that calcium affected the microenvironment within the colloid where the triglycerides reside. He proposed that the metal resinates (and salts of fatty acids) possibly migrate to the core of the colloid and so the effect predicted from the model may be more a result of changes in the internal structure of the wood resin colloids where the triglycerides reside.

CONCLUSIONS

Regression modelling of the effect of composition and other process variables on the deposition and colloidal stability of wood extractives from *P.radiata* resulted in models for the total amount of extractives, that are considered unreliable because of low correlations (low R^2) and poor fit with the test data. More reliable models were found if the individual components (resin acids, fatty acids and trigylcerides) were modelled individually. The models obtained showed that interactions between the components was occurring and that interactions between variables were important. Another key finding of the individual modelling of components was that opposing effects of variables on the different components was occurring which would help explain the poor models for the total extractives.

The main factors influencing deposition of the extractives were pH, DOM and composition (EAR). EAR and pH were also found to have the greatest influence on the stable colloids. The deposition models for the resin acids and triglycerides predicted a quadratic effect with pH suggesting that critical regions for high deposition at certain pH regions, which were dependent of the EAR and DOM levels, can occur. For the low EAR pulp which is known to be very susceptible to deposition, a maximum in deposition is predicted at pH levels below 5 in the absence of DOM but as DOM levels increase the maximum shifts to higher pH levels. This becomes quite critical for mill operations as this is in the operational region of the paper machine.

ACKNOWLEDGEMENTS

This research was funded by Norske Skog. The assistance of Adrian Wolfenden, Ahyoung Park and Naila Yaqoob, of the University of Tasmania, in helping to carry out the experimental work is greatly acknowledged. Matthew O'Connor, Norske Skog Albury, is also acknowledged for help in collecting the pulp samples.

REFERENCES

(1) Stack, K.R., Yaqoob, N., Ngwenya, E., Lewis, T.W. and Richardson, D.E. **-** Colloidal stability of Pinus radiata wood extractives Part 1: Effect of extractives composition and process variables. *Appita J*. **72**(1): 14 (2019).

(2) Richardson, D. E., Lee, R., Stack, K.R., Lewis, T.W. and Garnier, G. - Process factors affecting colloid stability and deposit formation in manufacture of newsprint from TMP and recycled fibre*, Proc. 66th Ann. Appita Conf.,* Melbourne, p48 (2012).

(3) Ekman, R. – Resin during storage and in biological treatment, in **Pitch control, wood resin and deresination,** Back E.L and Allen L.H. (Eds) Tappi, p192 2000.

(4) Strand, A., Sundberg, A., Vahasalo, L. and Holmbom B. - Influence of pitch composition and wood substances on the phase distribution of resin acid and fatty acids at different pH levels. *J.Disp. Sci.Tech*. **32**(5): 702 (2011).

(5) Qin, M., Hannuksela, T. and Holmbom B. - Deposition tendency of TMP resin and related model mixtures*. J. Pulp Pap Sci*. **30**(10): 279 (2004).

(6) McLean, D.S., Stack, K.R. and Richardson, D.E. - The effect of wood extractives composition, pH and temperature on pitch deposition*. Appita J*. **58**(1): 52 (2005).

(7) Sundberg, K., Thornton, J., Pettersson, C., Holmbom, B. and Ekman, R. – Calcium-induced aggregation of dissolved and colloidal substances in mechanical pulp suspensions. *J. Pulp Pap Sci.* **20**(11): J317 (1994).

(8) Sundberg, K., Thornton, J., Rainer, E. and Holmbom, B. - Interactions between simple electrolytes and dissolved and colloidal substances in mechanical pulp*. Nordic Pulp Pap Res J.* **9**(2): 125(1994).

(9) Lee, R., Stack, K.R., Richardson, D.E., Lewis, T.W. and Garnier, G. - Multi-salt coagulation of soft pitch colloids. *Colloids Surfaces A.* **409**: 74 (2012).

10) Sundberg, K., Thornton, J., Holmbom, B. and Ekman, R. - Effects of wood polysaccharides on the stability of colloidal wood resin. *J. Pulp Pap Sci*. **22**(7): J226 (1996).

11) Otero, D., Sundberg, K., Blanco, A., Negro, C., Tijero, J., and Holmbom, B. – Effects of wood polysaccharides on pitch deposition. *Nordic Pulp Pap Res*. **15**(5): 607 (2000).

12) Saarimaa, V., Vahasalo L., Sundberg, A., Pranovoch, A., Holmbom, B., Svedman, M. and Orsa, F. - Influence of pectic acids on aggregation and deposition of colloidal pitch. *Nordic Pulp Pap Res.* **21**(5): 613 (2006).

13) Stack, K.R., Lee R., Richardson, D. E., Lewis, T.W., and Garnier, G. - Complex formation and stability of colloidal wood resin pitch suspensions with hemicellulose polymers. *Colloids Surfaces A.* **441**:101 (2013).

14) Allen, L.H. – Pitch control- optimisation of alum usage in newsprint mills*. Pulp Pap Can*. **82**(11):143 (1981).

15) Allen., L.H and Douek, M. – Effectiveness of talc for pitch control in kraft pulp manufacture. *J. Pulp Pap Sci*. **19**(3): 131 (1993).

16) Sundberg, A., Ekman, R., Holmbom, B., Sundberg, K. and Thornton, K. Interactions between dissolved and colloidal substances and a cationic fixing agent in mechanical pulp suspensions. *Nordic Pulp Pap Res J*. **1**:226 (1993).

17) Truitt, R. E., Sennett, P.S and Allen, L.H. – Wood pitch deposition: Aluminium ions from Kaolin pigments. *Pulp Pap Can*. **97**(12): 99 (1996).

18) Willfor, S., Sundberg, A., Sihvonen, A.L. and Holmbom, B. – Interactions between fillers and dissolved and colloidal substances from TMP. *Paperi Ja Puu*, **82**(6): 398 (2000).

(19) Sundberg A., Strand, A., Vahasalo, L. and Holmbom, B. – Phase distribution of resin and fatty acids in colloidal wood pitch emulsions at different pH levels, *J Disp. Sci Technol*. **30**: 912 (2009).

(20) Nyren, V. and Back, E., The ionisation constant, solubility product and solubility of abietic and dehydroabietic acid. *Acta Chem. Scand*. **12**(7): 1516 (1958).

(21) Nyren, V. and Back, E., The ionisation constant, solubility product and solubility of lauric and myristic acid. *Acta Chem. Scand*. **12**(6): 1305 (1958).

(22) McLean D.S, Vercoe, D., Stack. K. and Richardson, D.- The colloidal pKa of lipophilic extractives commonly found in Pinus radiata, *Appita J*. **58**(5): 362 (2005).

(23) Qin M., Hannuksela, T. and Holmbom, B. – Physico-chemical characterisation of TMP resin and related model mixtures. *Colloids Surfaces A*, **221**:243 (2003).

(24) Blanco, A., Dahlquist, E., Kappen, J., Manninen, J., Negro, C. and Ritala, R., Use of modelling and simulation in the pulp and paper industry, *Mathematical and Computer Modelling of Dynamical Systems* **15**(5): 409 (2009).

(25) Stack, K.R., Stevens, E.A., Richardson, D.E, Parsons, T and Jenkins, S.- Factors affecting the deposition of pitch in process waters and model dispersions, *52nd Appita Ann Gen. Conf*, Brisbane May 11-15 (1998) p59.

(26) Vercoe, D, Stack, K.R., Blackman, A., Yates, B and Richardson, D.E. – An innovative approach characterising the interactions leading to pitch deposition, *J. Wood Chem. Technol*. **24**(2): 115 (2004).

(27) Dreisbach, D.D. and Michalopoulos, D. L.- Understanding the behaviour of pitch in pulp and paper mills, *Tappi J.* **62**(6):129 (1989).

(28) Stack, K.R., Lee, R., Zhang, J., Lewis, T.W., Garnier, G. and Richardson, D E. - Colloidal and deposition behaviour of Pinus Radiata extractives and model colloid systems, *Proc. 16th ISWFPC*, Tainjin, China 8-10 June 2011, p1143.

(29) Strand, A., Sundberg, A., Vahasalo, L and Holmbom, B.- Destabilisation of colloidal wood pitch by calcium ions in TMP suspensions, *Proc. 16th ISWFPC*, Tainjin, China 8-10 June 2011, p1223.

(30) Lee, R., Stack, K.R., Lewis, T., Garnier, G., Richardson, D.E., Ottaviani, M. F., Jockusch, S. and Turro, N.J.- Structure of wood extract colloids and effect of CaCl2 on the molecular mobility, *Nordic Pulp Pap. Res. J.* **27**(3): 639 (2012).

Submitted to Appita Journal 27 Nov 2018, accepted 6 March 2019

APPENDIX

Appendix 1: Equations of the predicted models found from the regression modelling not displayed in text of paper.

Dependant Variable	Predicted equation	R^2	RMSE
RA - stable colloids [mg/L]	=0.067Predeposition concentration[mg/L] -56A + 7.6D - 0.19E -0.019(AxC) +4.3(AxD) +0.41(BxE) -0.000062C^2 +0.0063(CxD) -0.88D^2+0.78 FA (in stable colloids) **[mg/L]** +0.93TG (in stable colloids) **[mg/L]**	0.97	6.0
TG- stable colloids [mg/L]	=0.084Predeposition concentration[mg/L] +38A -0.033C - 3.8D -0.27E -1.3(AxB) +0.0238(AxC) +0.13(BxD) -0.29(BxE) +0.000084C^2 -0.0025(CxD) +0.23D^2 +0.053(DxE) +RA (in stable colloids) **[mg/L]**	0.97	4.0
FA - stable colloids [mg/L]	=3.6D +0.12E -6.1(AxD) -0.26(BxD) -0.31(BxE) -0.014(CxD) +0.46(AxBxD) -0.051(DxE) +0.0016(AxCxD) +0.096(AxDxE) +0.22RA (in stable colloids) **[mg/L]**	0.92	3.0
RA-unstable colloids [mg/L]	= 22A -0.56D +0.095E -0.36(AxB) -1.3(AxD) -0.23(AxE) +0.0005(CxD) +2.0FA (in unstable colloids) **[mg/L]** +0.26TG(in unstable colloids) **[mg/L]**	0.81	3.0
TG-unstable colloids [mg/L]	= 0.26D +0.022(AxC) -0.000037C^2 +0.0002(CxE) -0.008(DxE) -0.096(AxBxD) -0.019(AxBxE) +0.69FA (in unstable colloids) **[mg/L]** +0.26 RA (in unstable colloids) **[mg/L]**	0.58	3.2
FA- unstable colloids [mg/L]	=-4.0A -0.16B +0.0046C +0.02D +0.35(AxB) -0.0074(AxC) +0.025(AxE) +0.18RA (in unstable colloids) **[mg/L]** +0.066TG (in unstable colloids) **[mg/L]**	0.80	0.09
RA- soluble fraction [mg/L]	= 0.062Predeposition concentration[mg/L] +36A -0.031C - 4.5D -0.25E +0.039(AxC) -1.1(AxD) -6.5(AxD) +0.029(BxE) +0.00010C^2 -0.0059(CxD) + 0.77D^2 -0.0040(DxE) +0.91FA (in soluble fraction) **[mg/L]** +0.95TG(in soluble fraction) **[mg/L]**	0.90	5.0
TG- soluble fraction [mg/L]	= -0.020Predeposition concentration[mg/L] +0.74D - 0.012(AxC) +0.12(AxE) +0.0073(CxD) -0.069D^2 -0.0092(DxE) +0.30FA (in soluble fraction) **[mg/L]** +0.18RA(in soluble fraction) **[mg/L]**	0.59	2.3
FA-soluble fraction [mg/L]	=0.33B +0.079E -0.51(AxB) +0.87(AxD) -0.19(AxE) +0.000005C^2 -0.063D^2 +0.13RA (in soluble fraction) **[mg/L]** +0.21TG(in soluble fraction) **[mg/L]**	0.59	1.9

Key: A= EAR; B=DOM:WE ratio; C=Ca [mg/L]; D=pH; E= temperature [°C]